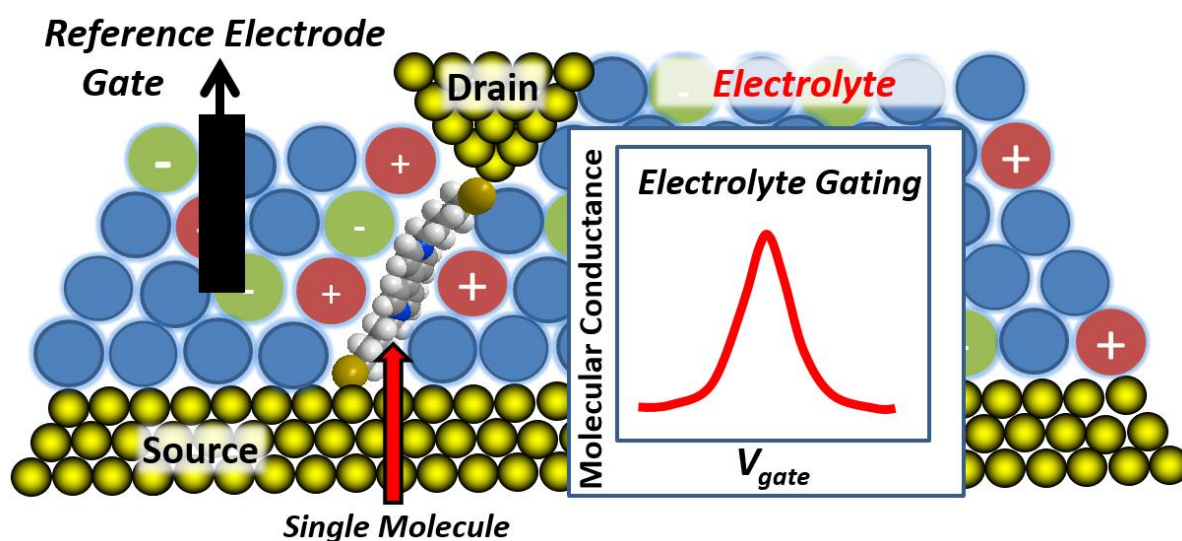


## Single Molecule Nanoelectrochemistry in Electrical Junctions

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### CONSPECTUS



It is now possible to reliably measure single molecule conductance in a wide variety of environments including organic liquids, ultra-high vacuum, water, ionic liquids and electrolytes. The most commonly used methods deploy scanning probe microscopes, mechanically formed break junctions or lithographically formed nano-gap contacts. Molecules are generally captured between a pair of facing electrodes and the junction current response is measured as a function of bias voltage. Gating electrodes can also be added so that the electrostatic potential at the molecular bridge can be independently controlled by this third non-contacting electrode. This can also be achieved in an electrolytic environment using a four-electrode bipotentiostatic configuration which allows independent electrochemical potential control of the two contacting electrodes. This is commonly realized using an electrochemical STM and enables single molecule electrical characterization as a

function of electrochemical potential and redox state of the molecular bridge. This has emerged as a powerful tool in modern interfacial electrochemistry and nanoelectrochemistry for studying charge transport across single molecules as a function of electrochemical potential and the electrolytic environments. Such measurements are possible in electrolytes ranging from aqueous buffers to non-aqueous ionic liquids.

In this article we illustrate a number of examples of single molecule electrical measurements under electrochemical potential control use a scanning tunneling microscope (STM) and demonstrate how these can help in the understanding of charge transport in single molecule junctions. Examples showing charge transport following phase coherent tunneling to incoherent charge hopping across redox active molecular bridges are shown. In the case of bipyridinium (or viologen) molecular wires it is shown how electrochemical reduction leads to an increase of the single molecule conductance, which is controlled by the liquid electrochemical gating. This has been referred to as to a “single molecule transistor configuration” with the gate voltage being provided by the controllable potential achieved through the electrochemical double layer. It is shown how the electrolyte medium can control such gating, with ionic liquids providing more efficient gate coupling than aqueous electrolytes. Control of the conductance of viologen molecular wires can also be achieved by encapsulating the viologen redox moiety within a molecular cage, thereby controlling its immediate environment. Molecular conductance can also be gated through multiple redox states. This has been shown for the redox moiety pyrrolo-tetrathiafulvalene which undergoes single molecule electrochemical transistor gating through three redox states in molecular junctions. Charge transport through this junction follows a 2-step hopping mechanism, demonstrating the role of the redox center in electron transfer across the molecular bridge. Recent electrolyte gating studies of rigid, conjugated redox-active metal complexes with tailored terpyridine coordinating ligands and anchors are also presented. These aforementioned studies have all been performed with gold electrode contacts.

The article concludes with recent data showing that it is now possible to study single molecule electrochemical gating with nickel electrodes. This opens up new perspectives for studying interfacial charge transfer with a wide variety of other electrode materials including semiconductor electrodes and also points towards future opportunities for coupling molecular spintronics and nanoelectrochemistry.

Nanoelectrochemistry emerged and developed as a distinct branch of electrochemistry in the later 1990s and 2000s. With its focus on the electrochemical properties of materials at the nanometer size regime, it has relevance to practically every branch of electrochemistry. Nanoelectrochemistry has encompassed electrochemical investigations of newly-emerged nanomaterials, for example metal, oxide and semiconductor quantum dots and nanoparticles, carbon nanomaterials such as nanotubes and, more recently, graphene. New techniques and platforms for probing the nanoscale have also emerged, for example nanopores and nanometer-sized electrodes. An important nanoelectrochemical technique to emerge, which forms the basis of this account, is the ability to study the electrical properties of single redox-active molecules in nano-electrical junctions. This can be applied in electrochemical environments, ranging from aqueous electrolytes to ionic liquids, under full electrochemical control. This has given electrochemists the ability to study charge transfer across single molecules as a function of the electrode potential and environment, giving new insights into electrochemical charge transfer mechanisms at the nanoscale. In this account, following an introduction to the techniques for the electrochemical (or electrolyte) gating of single molecules, we focus on key work from our group and our collaborators on this topic.

The concept of measuring the conductance of single molecules in an electrochemical environment is shown in Figure 1. The molecular bridge is attached between two facing metallic electrodes separated by nanometer dimensions. Attachment is usually through chemisorption groups at either end of the molecule. In this way electrical properties of the molecular junction can be measured through application of a bias voltage. Additional electrodes are needed in order to control the electrode potential. The contacting electrodes serve as working electrode 1 and 2, respectively, while counter and reference electrodes are placed remote from the nano-gap. This is a four-electrode bipotentiostatic configuration which allows independent potential control of the two working electrodes, as commonly used in in-situ electrochemical STM. In this way the electrode potential can be changed while the bias voltage between the contacting electrodes is maintained at a constant potential.

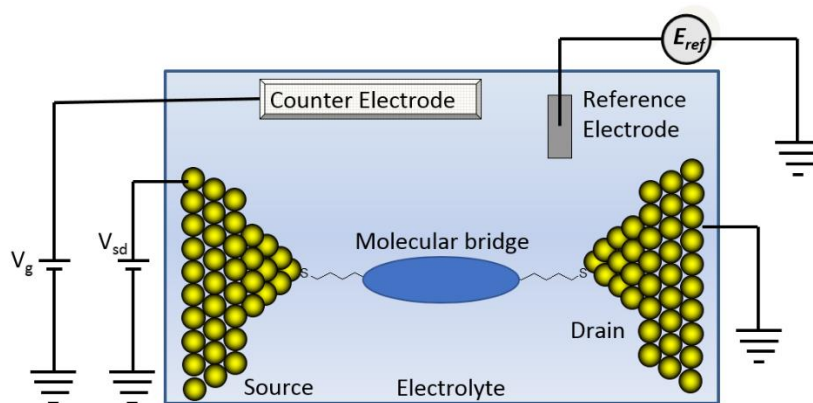


Figure 1. A schematic illustration of a single molecule wire in an electrical junction under electrochemical conditions. Reprinted with permission from ref. <sup>1</sup>. Copyright 2012 American Chemical Society.

In Figure 1 the two contacting electrodes have been labeled as source and drain, while a “gating voltage” ( $V_g$ ) is achieved through the counter electrode / reference electrode combination. In this way it is clear that the molecule is placed in what is equivalent to a “single molecule transistor configuration” with the gate voltage being provided by the controllable potential achieved through the electrochemical double layer. These have also been referred to as “single molecule field effect transistors” (FETs). Single molecules can also be assembled into nano-fabricated solid-state junctions with source-drain separation controllable to sub-nanometer precision, and a third underlying electrode which acts as a back-gate.<sup>2</sup> This back-gate can, for instance, be separated physically from the molecular junction by an intervening dielectric such as  $\text{SiO}_2$  but still enables electrostatic control at the molecule through application of the gate voltage. However, these 3-terminal solid-state platforms can be difficult to fabricate, and there is no control over the degree of gate coupling to the molecule from device to device. On the other hand liquid electrochemical gating can be both efficient, reliable and has the ability, given an appropriate electrode/electrolyte combination, to achieve gating over relatively large voltage ranges.

The most commonly used methods for single molecule electrical measurements under electrochemical control use a scanning tunneling microscope (STM) and these are adapted from 2-

terminal single molecule techniques with no electrochemical control. Typically, gold tips and substrates are employed in the formation of gold | molecule | gold electrical junctions. The STM can be used in either a “contact” or “non-contact” fashion to form the junctions. The former method, known as the in-situ break junction (BJ) technique,<sup>3</sup> is illustrated in Figure 2. In this method, the STM tip is first directed into metallic contact with the gold surface. During withdrawal of the tip, a single gold point contact is formed (step 2 in Figure 2), which gives a conductance plateau at  $1G_0$  ( $G_0$  is the quantum unit of conductance, given by  $2e^2/h$ ; 77  $\mu\text{S}$ ). As the tip is retracted further, this gold bridge breaks to leave an open nano-gap into which single or small groups of molecules can adsorb, as illustrated here for 4,4'-bipyridine (Step 3, Figure 2).<sup>3</sup> Typically, the conductance drops at this stage from  $1G_0$  to several orders of magnitude lower or less; for instance the conductance of a gold-bipyridine-gold single molecule junction is  $\sim 10^{-3} G_0$  while that for a gold-1,8-octanedithiol-gold single molecule junction is a further 2 orders of magnitude lower. As the tip is retracted further, the molecular junction itself breaks, whereupon the junction current abruptly falls. As a result, the junction conductance is typically high at close tip-to-substrate separations, with tilted molecular bridges in the junctions. This evolves into a current plateau as the tip is further retracted with a rather abrupt end to the plateau as the molecular junction breaks. Many of these current-distance traces are compiled together in current or conductance histograms, with the plateau features manifesting as peaks in the histograms which correspond to favored junction conductance values.<sup>3</sup> Multiple peaks in the histogram can correspond to integer numbers of molecules in the junction or different binding geometries associated with the surface anchoring groups. Examples of current-distance retraction curves and histograms obtained by the BJ method by the Tao group are shown in Figure 3 (these data were obtained in 0.1 M  $\text{NaClO}_4$  solutions under electrochemical conditions at -0.2 V vs. Ag/AgCl).<sup>4</sup> Figure 3a and b show data corresponding to the gold-atomic point contact stage with clear current plateaus at  $1G_0$  and a histogram peak at  $G_0$  (peaks at 2 and 3  $G_0$  are also marked and these are related to multiple rather than single point contacts). At the molecular junction stage of tip retraction, current plateaus and conductance histogram peaks are seen at  $\sim 10^{-2} G_0$  for

benzenedithiol (BDT) molecular junctions (Figure 3c and d), and  $6 \times 10^{-4} G_0$  for the longer and less conjugated molecule benzenemethanedithiol (BMDT, Figure 3e and f).<sup>4</sup>

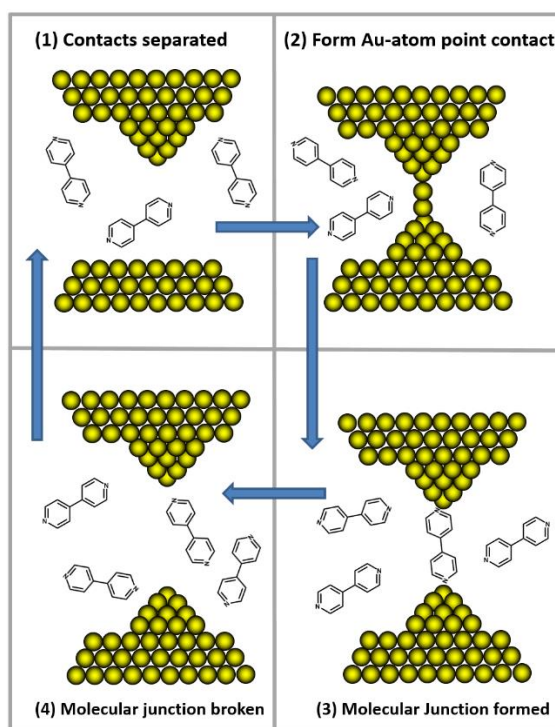


Figure 2: An illustration of the in-situ BJ method for molecular junction formation with an STM.

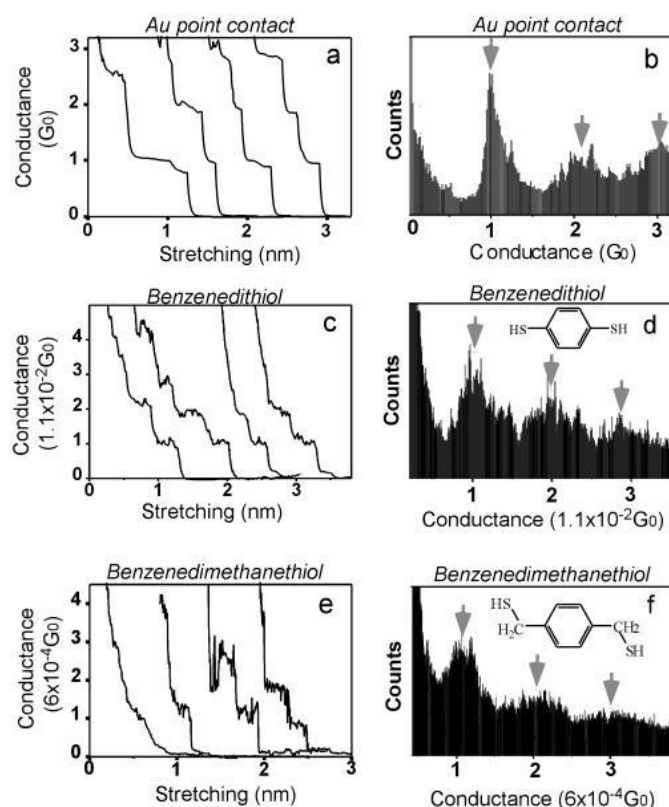


Figure 3: Conductance versus distance traces recording during BJ experiments showing conductance histograms of gold point contact (a, b) and BDT molecular junctions (c, d) and BDMT junctions (e, f) measured under electrochemical conditions at -0.2 V vs. Ag/AgCl in 0.1 M NaClO<sub>4</sub> solutions. For clarity the conductance traces have been displaced on the x-axis.<sup>4</sup> Reprinted with permission from ref. <sup>4</sup>. Copyright 2012 American Chemical Society.

Molecular junctions can also be formed without the need to first form a metallic point contact. This can be achieved by the so-called  $I(s)$  method developed in our laboratories,<sup>5</sup> where  $I$  is current and  $s$  is retraction distance of the STM tip. Here the STM tip is approached close to the substrate surface. Under such conditions, target molecules can stochastically bridge the gap between the tip and surface.<sup>5,6</sup> If the STM tip is then retracted, simple current-distance molecular junction curves resembling those obtained for the BJ method can result. Figure 4 schematically illustrates the  $I(s)$  technique with conductance distance curves in the presence of a molecular junction (upper curve) and in its absence (lower curve). The tip approaches the surface and molecular junction formation



can occur (A-B), the molecule is then extended in the junction as the tip retracts (C-D) but the molecular junction breaks and the current decays rapidly resulting in a current step.

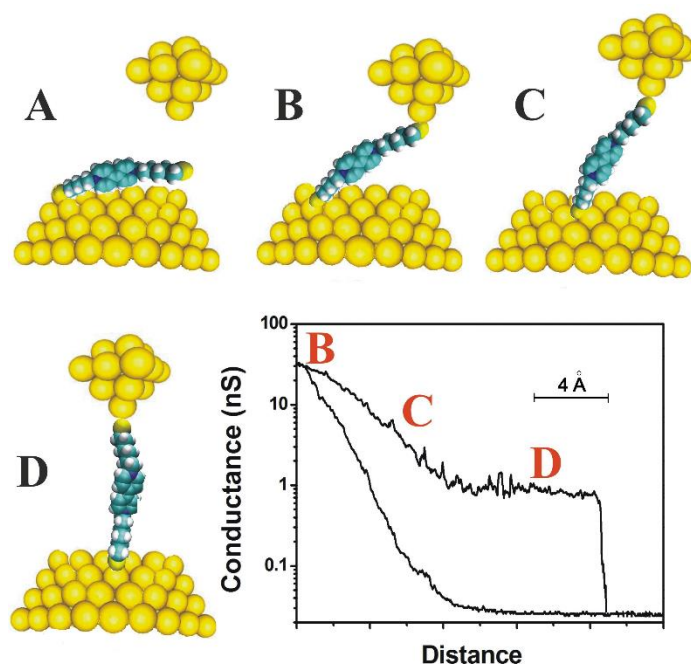


Figure 4. A schematic representation of the  $I(s)$  STM technique for molecular junction formation, showing four stages of the molecular junction formation (A-D) and corresponding conductance-distance curves with stages B-D labelled. The lower curve shows the conductance-distance response in the absence of molecular bridge formation. Reproduced from ref. <sup>7</sup> with permission from the PCCP Owner Societies.

Other methods exist for determining single molecule conductance under electrochemical conditions. In the  $I(t)$  method, the STM tip is positioned at constant height, close to the metal surface covered with the adsorbed target molecule.<sup>6</sup> In this configuration, molecular bridges between the STM tip and surface form intermittently, giving rise to current jumps or “blinks”. These jumps can be accumulated and analyzed to give molecular conductance.<sup>6</sup> This method has also been combined with ac small amplitude mechanical modulation of the STM tip distance.<sup>8</sup> The ac response can be used to recognize the presence of a bridging molecule, while the DC junction current is used to quantify the molecular conductance.<sup>8</sup> Current-voltage traces can also be recorded either during a

current blink or in an automated fashion during tip retraction while a molecular junction is in place. An alternative method for forming junctions is the so-called “jump-to-contact” method. In this method a foreign metal is electrochemically plated on the STM tip.<sup>9-11</sup> This metal can be transferred from the STM tip to the substrate as the STM tip is rapidly approached and retracted from the surface under bipotentiostatic electrode potential control. This is a very interesting technique since it allows the formation of metal-molecule-metal electrical junctions from a wide variety of metals which can be electrodeposited such as Ag, Cu and Pd.<sup>9-11</sup>

The first studies of redox active single molecule wired electrical junctions (with the molecular target directly tethered by chemisorption between two metallic contacts) were performed by Haiss et al.<sup>5</sup> Bipyridinium or viologen ( $V^{2+}$ ) molecular wires were the focus of this study with the  $V^{2+}$  moiety being readily electrochemically reduced to its radical cation form  $V^{\cdot+}$  in aqueous electrolytes. The reduction of the viologen molecular wire contacted in a single molecular junction is schematically shown in Figure 5. The molecular bridge is connected at both end to the gold electrodes (the STM tip and gold substrate, respectively) through thiol anchoring groups. Such chemisorption end groups have been referred to as “molecular alligator clips” for electrically wiring the molecule into the junction. Notice here also, that the central viologen group is separated from the contacts by  $-S(CH_2)_6$  spacers; the shorthand notation adopted for this molecule is “6V6” with the “6” representing the  $-S(CH_2)_6$  linkers and the “V” the central viologen moiety. These spacers act to ensure that the viologen moiety is not directly electronically coupled to the gold contacts, thereby promoting electrochemical charge hopping type modes of electron transfer across the junction when the electrode potential of the metal contacts is brought close to the reversible potential for the redox couple (see later). Figure 6 shows the dependence of single molecular conductance on electrode potential, here plotted as the overpotential.<sup>5</sup> Each point of this plot is obtained from an individual conductance histogram recorded for many  $I(s)$  junction formation processes. The conductance increases as the reversible potential is approached from positive overpotentials and reaches a plateau at negative overpotential. Over this electrode potential range the conductance increases by around six-fold as a

result of the electrochemical gating. It is notable however that the conductance rise as the electrode potential is made more negative is slow and has a sigmoidal shape rather than a bell-shaped curve which would be expected for electrochemical hopping mechanisms discussed later in the text. This slow rise of conductance with electrode potential has been referred to as “soft gating” and this is described further below.

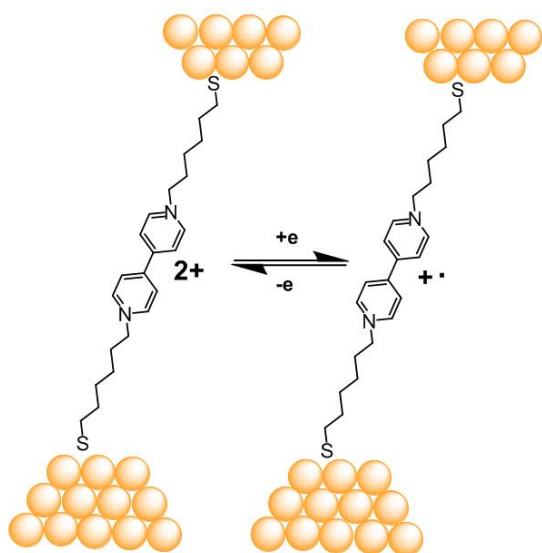


Figure 5. An illustration of electrochemical switching in an electrical junction of the viologen bridge (6V6) from its dication to cation radical state.

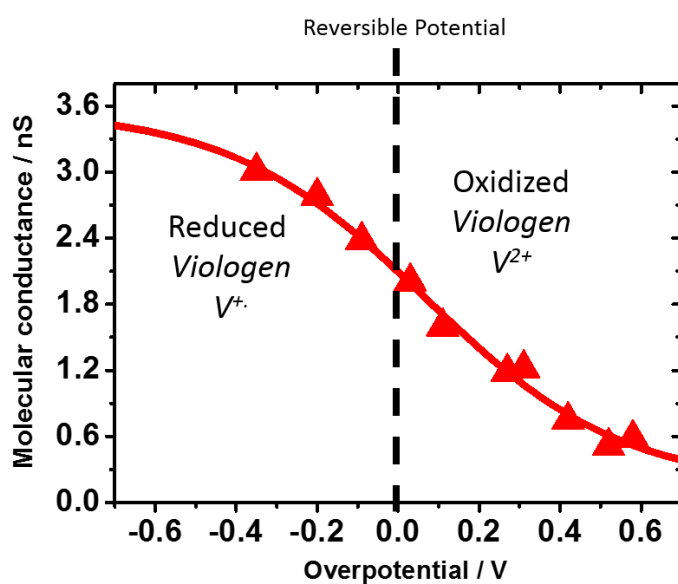


Figure 6. Single molecule conductance of a viologen molecular bridges (6V6) versus electrochemical overpotential. The conductance increases in a sigmoidal fashion as the electrode potential is made more negative. Adapted from ref. <sup>12</sup>. Copyright 2008 American Chemical Society.

The data for the viologen system shown in Figure 6 was recorded with aqueous electrolytes.<sup>5</sup> More recently, ionic liquids have been employed for such measurements on a variety of molecular redox systems, including viologens,<sup>13</sup> pyrrolo-tetrathiafulvalene<sup>1</sup> and conjugated redox-active metal complexes<sup>14</sup>. Ionic liquids were first used for electrochemical scanning tunneling spectroscopy studies on redox active monolayers,<sup>15</sup> but it was later established that they can also be used for single molecule wire studies.<sup>16</sup> Single molecule data for the electrochemical gating of 6V6 in ionic liquids (Figure 7) starkly contrasts to data for the same molecule gated in aqueous electrolytes (Figure 6).<sup>13</sup> In ionic liquids a bell shaped profile is observed, with the conductance being in a high state around zero overpotential and low at both sufficiently negative and positive overpotentials respectively.<sup>13</sup> The peak at close to zero overpotential is a strong indication that charge transfer across the molecular bridge occur by a 2-step electrochemical hopping-type mechanism rather than a resonant electron transfer, since the latter mechanism predicts that the conductance peak is shifted by the reorganization energy away from zero overpotential.<sup>17-19</sup> A description of the resonant electron transfer model and the reason for this shift away from zero overpotential is given in a separate review <sup>19</sup>.

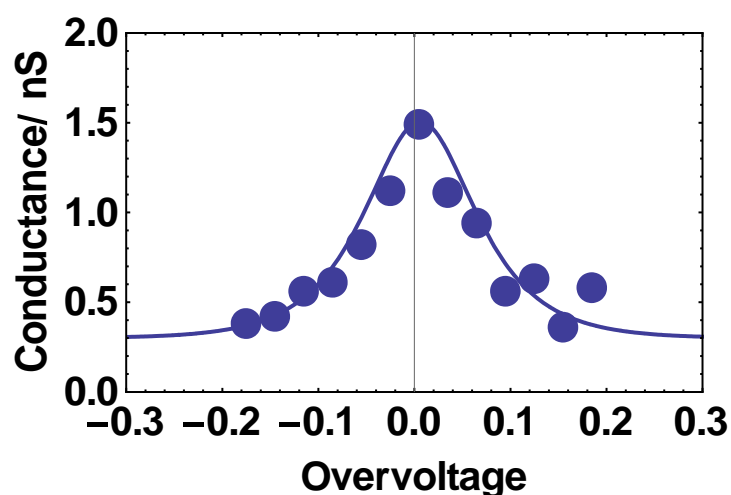


Figure 7. Single molecule conductance for a viologen molecular bridge (6V6) recorded as a function of electrochemical overpotential in ionic liquid electrolytes. Reprinted from ref. <sup>13</sup>. Copyright 2015 American Chemical Society.

The electrochemical gating behavior shown in Figure 7 has been interpreted with a “two-step electrochemical hopping mechanism” from Kuznetsov and Ulstrup which is illustrated in Figure 8. This illustration shows the gold contacts at either side, with electron transfer to/from the Fermi levels of these electrodes. Following pre-organization of the molecule and environment to enable a Frank-Condon electronic transition, the electron transfer occurs onto the viologen group in the center of the nano-gap, marked as Step (1) in this figure. This is an electrochemical reduction with a rate constant  $k_a$ . In the two-step adiabatic model, relaxation occurs (step 2) followed by electron

$$k_a \approx \frac{\omega_{eff}}{2\pi} \exp \left[ -\frac{[\lambda - e\eta - \gamma e V_{bias}]^2}{4\lambda k_B T} \right]$$

$$k_b \approx \frac{\omega_{eff}}{2\pi} \exp \left[ -\frac{[\lambda + e\eta - (1-\gamma)e V_{bias}]^2}{4\lambda k_B T} \right]$$

transfer to the Fermi level of the other contact (step 3, electrochemical rate constant,  $k_b$ ). As relaxation occurs (step 2) many electrons can transfer through the molecular junction in a “cascade” which gives rise to the current amplification seen in the conductance-overpotential relation in Figure 7. The process is characterized by the two electrochemical rate constants,  $k_a$  and  $k_b$  which have the following form: <sup>20</sup>

Here  $\omega_{eff}$  is a characteristic nuclear vibrational frequency,  $e$  is the electron charge,  $\eta$  is the electrochemical overpotential,  $k_B$  is Boltzmann’s constant,  $T$  the temperature,  $\lambda$  is the reorganization energy and  $V_{bias}$  is the bias voltage between the STM tip and substrate. The parameters  $\gamma$  is the fraction of the bias voltage experienced at the site of the redox center. From these two rate constants, the steady-state current flowing across a symmetrical molecular junctions is given in the adiabatic (strong coupling) limit by:<sup>20</sup>

$$i_{tunn}^{strong} = 2en_{el} \frac{k_a k_b}{k_a + k_b}$$

Where  $n_{el}$  is the number of electrons transferred through the junction during the relaxation step

(step 2 in Figure 8). The full form of the Kuznetsov Ulstrup equation<sup>20</sup> is:

$$j_{enh} \approx j_0 \exp\left(-\lambda/4kT\right) \frac{\exp(e|V_{bias}|/4kT)}{\cosh\left(\frac{e(0.5-\gamma)V_{bias}-e\xi\eta}{2kT}\right)}$$

This equation describes the enhanced current ( $j_{enh}$ ) flowing across the molecular junction. An expression for  $j_0$  is given in <sup>20</sup> and  $\xi$  is the fraction of the electrode potential experienced at the redox site. Through application of this equation, values for the reorganization energy and the fraction of the electrochemical potential drop experienced at the redox site can be obtained.

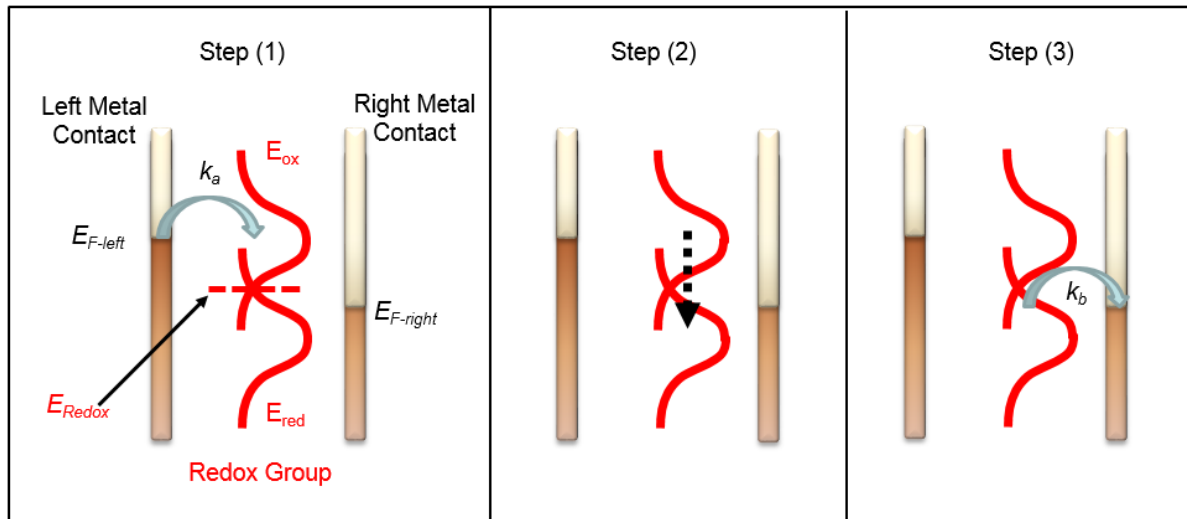


Figure 8. The two-step electrochemical hopping mechanism of charge transfer through a redox active single molecular junction.

The slow and broad rise of the conductance as the electrode potential is made negative for 6V6 molecular junctions in aqueous electrolytes (Figure 6), giving the absence of a maximum, was initially ascribed to configurational fluctuations influencing the charge transport mechanism.<sup>21</sup> A model involving both superexchange-based electron transport and pre-organization of the molecular bridge was proposed for this 6V6 system, rather than a sequential electron transfer process. In this

model, the molecular bridge must reach, through pre-organization, molecular configurations in which electron tunneling is more facile. In other words, both the molecular nuclear coordinates and the environment pre-organize to produce a configuration in which electron tunneling is more facile.<sup>21</sup> In this 'soft gating' model, the redox active viologen center is not reduced over the range of overpotentials represented in Figure 6. More recently, with the ability to perform single-molecule electrochemical gating in ionic liquid, we have turned our attention to the influence of ionic liquids on charge transport across the viologen bridge.<sup>13</sup> Figure 9 shows comparative data for 6V6 recorded in aqueous and ionic liquid electrolytes and it is notable how much the charge transport patterns change between these two environments. The analysis in Figure 9 is based on the 2-step KU model ("electrochemical hopping type model") being operative in both aqueous and ionic liquid media and differs from previous work<sup>21</sup> which had used a superexchange model to describe electron transport across the viologen bridge in aqueous environments. Using this model the key differences between the two environments are in the reorganization energies and in the parameter  $\xi$ , which is the fraction of the electrode potential experienced at the viologen redox center. The reorganization energies ( $\lambda$ ) computed from these data for the aqueous environment is substantially lower than that found for the ionic liquid electrolytes. The high value for the ionic liquid environment reflects the reorganization of these generally highly structured liquids within the nano-gap environment between the STM tip and metal substrate.<sup>13</sup> The high reorganization energy of the ionic liquid consequently leads to a decreased junction conductance (Figure 9). The data shown in figure 9 for 6V6 in ionic liquid yields  $\xi=1$ , corresponding to 100 % of the applied electrode potential being experienced at the viologen redox center.<sup>13</sup> This shows that ionic liquid electrolytes are highly effective media for single molecule electrolyte gating. Indeed, gating efficiency for such liquid electrolyte single molecule transistor configuration generally greatly exceeds what is achievable in solid-state 3-terminal platforms created using nanolithography.<sup>13</sup> On the other hand the aqueous data in Figure 9 gives a low gating parameter  $\xi$  of 0.2, which means that only 20 % of the applied electrode potential is experienced by the viologen moiety in the Au|6V6|Au nanogap.<sup>13</sup>

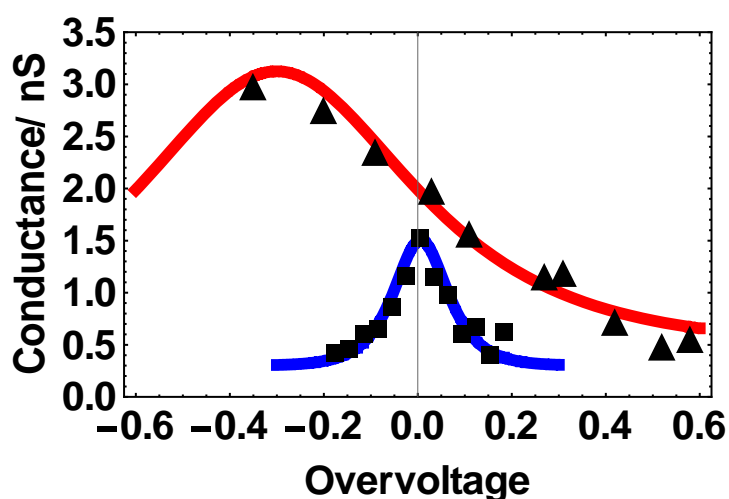


Figure 9. Single molecule conductance for a viologen molecular bridge (6V6) recorded as a function of electrochemical overpotential in aqueous (red line and triangles) and ionic liquid electrolytes (blue line and squares). Reprinted from ref. <sup>13</sup>. Copyright 2015 American Chemical Society.

Single molecule electrochemical gating data for 6V6 shows the impact of the liquid environment on controlling charge transport across these molecular electrical junctions.<sup>22</sup> Recently, we have devised another chemical method for controlling the immediate environment of the viologen moiety in the nano electrical junction. This was achieved by threading the 6V6 viologen wire within a cucurbit[8]uril CB[8] host (Figure 10). The local microenvironment within the cavity leads to an increase in the single molecule conductance of 6V6. This is consistent with the 2-step electrochemical hopping model and it is envisaged that the conductance increase is a result of lowering of the solvent (water) reorganisation energies of “high energy” water surrounding the viologen group and encapsulated with the host.

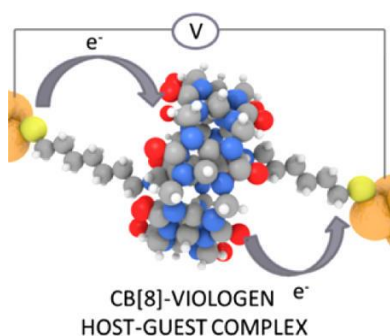




Figure 10. A schematic illustration of electron transport through a viologen-cucurbit[8]uril supramolecular complex. The viologen redox moiety is threaded within the CB[8] host which controls the environment surrounding the viologen guest. Reprinted from ref. <sup>22</sup>. Copyright 2016 American Chemical Society.

Ionic liquids also offer the opportunity to extend the potential window beyond what can be usually achieved with aqueous electrolytes. This had been put to effect in the study of the redox active molecular bridge containing the redox moiety pyrrolo-tetrathiafulvalene (pTTF).<sup>1</sup> In particular the molecular bridge 6pTTF6 has been studied, which possesses  $-S(CH_2)_6$  linkers on either end of the pTTF group. In aqueous electrolytes only the first oxidation of this moiety could be studied,<sup>12</sup> while in ionic liquids 3 redox states could be accessed, with oxidation of pTTF to both its cation and dication state. This is apparent from monolayer voltammetry of self-assembled monolayers on gold electrodes (Figure 11). The electrode potential dependence of the single molecule conductance is shown in figure 12, with the conductance rising at the reversible potential for the first oxidation and rising again at the second oxidation. These data have been fitted to the Kuznetsov Ulstrup 2-step hopping model showing the role of the pTTF redox center in electron transfer across the molecular bridge.<sup>1</sup> As for the viologen system high values of the gating parameter  $\xi$  are obtained for these data in ionic liquids.<sup>1</sup>

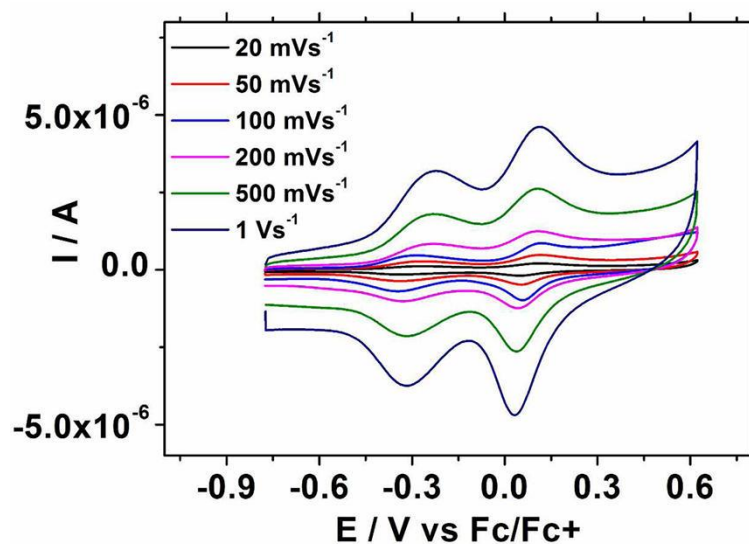


Figure 11. Cyclic voltammograms for self-assembled monolayers of 6pTTF6 recorded on Au(111) in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMOTf) at the marked sweep rates. These show two oxidation waves,  $6\text{pTTF6} \rightarrow 6\text{pTTF6}^+$  and  $6\text{pTTF6}^+ \rightarrow 6\text{pTTF6}^{2+}$ , respectively. Reprinted from ref. <sup>1</sup>. Copyright 2012 American Chemical Society.

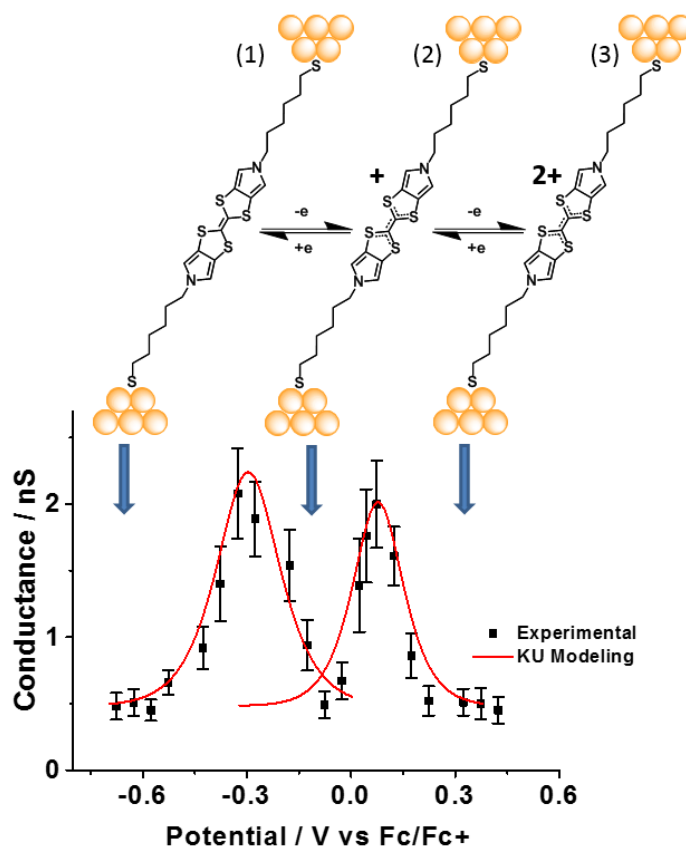


Figure 12. Single molecule conductance for the illustrated pyrrolo-tetrathiafulvalene (pTTF) molecular bridge recorded as a function of electrochemical overpotential in ionic liquid electrolyte. Single molecule electrochemical transistor gating is shown through the illustrated three redox states of the molecular junction. Reprinted from ref. <sup>1</sup>. Copyright 2012 American Chemical Society.

There has recently been much interest in transition metal-containing molecular wires, particularly those in which oligo(phenyleneethynylene) units are used to connect organometallic metal centers to electrodes via terminal contact groups. However, to date none of these has been suitable for a detailed conductance-overpotential study owing to insufficiently-reversible redox chemistry. To test the conductance-overpotential relationship for related rigid, conjugated redox-active metal complexes, we have examined the complexes  $[M(\text{pyterpy})_2]^{2+/3+}$  ( $M = \text{Co, Fe}$ ;  $\text{pyterpy} = 4'-(\text{pyridin-4-yl})-2,2':6',2''\text{-terpyridine}$ ).<sup>14</sup> For these measurements we took advantage of the wide redox window afforded by ionic liquids; the  $M(\text{II})/M(\text{III})$  redox potential for  $[\text{Fe}(\text{pyterpy})_2]^{2+/3+}$  in particular was +0.78 V vs. ferrocene/ferrocenium. We found that under these conditions, the conductance-overpotential relationships for both metal complexes (Figure 13) were very similar to those of pTTF (above); the behavior could likewise be fitted to the Kuznetsov-Ulstrup model, with fitting parameters of  $\lambda = 0.80$  eV,  $\xi = 0.5$ ,  $\gamma = 0.40$  for the Co complex, while those for the iron complex were  $\lambda = 0.77$  eV,  $\xi = 0.8$  and  $\gamma = 0.55$ . The reorganization energies for  $[M(\text{pyterpy})_2]^{2+/3+}$  are notably lower than for either the viologens or pTTF (1.3 and 1.2 eV respectively), while the degree of gate coupling experienced by the metal complexes is also lower, indicating that the screening is not so effective. This may be due to the metal-centered redox orbitals being better shielded by the surrounding ligand 'shell'.

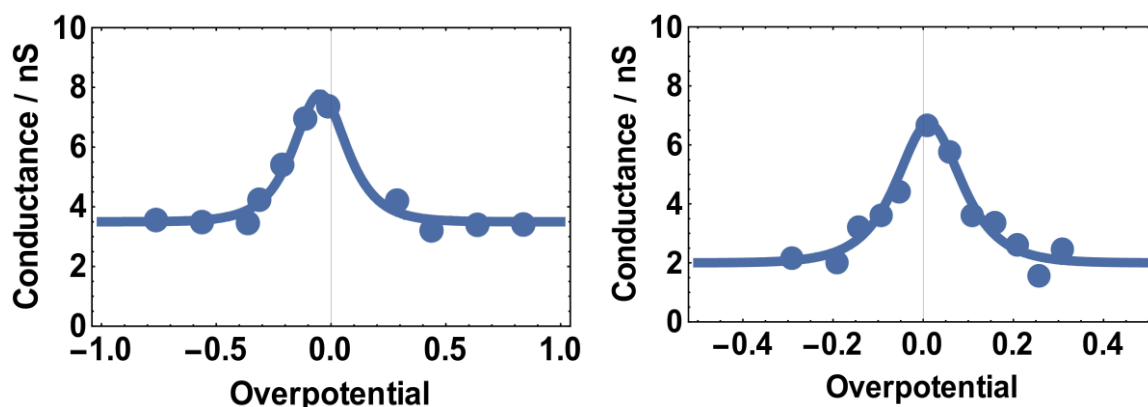


Figure 13. Conductance–overpotential plots for (a)  $[\text{Co}(\text{pyterpy})_2]^{2+/3+}$  and (b)  $[\text{Fe}(\text{pyterpy})_2]^{2+/3+}$  in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM TFSI). Data at each potential shown as points; the line corresponds to the fitting to the Kuznetsov-Ulstrup model, q.v. ref. <sup>14</sup>.

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As part of a study aimed at addressing the question of whether there is a correlation between molecular junction conductance and electrochemical rate constant for redox-active molecules, Zhou et al had earlier investigated the conductance-overpotential relationship for  $[\text{Os}(\text{pyterpy})_2]^{2+}$  (isoelectronic with  $[\text{Fe}(\text{pyterpy})_2]^{2+}$ ) over its Os(II)/Os(III) redox wave. Using an aqueous electrolyte (0.1 M  $\text{NaClO}_4$ ), they determined a broad, sigmoidal conductance increase, from 2.1 nS for the Os(III) redox state to 17.8 nS for the Os(II) state, reminiscent of the behavior we earlier observed for viologens in aqueous media (although in this electrolyte, over the timescale of molecular conductance determination experiments, the Os(II)/Os(III) voltammetry was not fully electrochemically reversible).<sup>23</sup> As in the case of the viologens, this is an example of the conductance-overpotential relationship being governed more by the medium than by the molecular structure. However, the molecular structure evidently also plays a role, as is clear from the behavior of pTTF in both aqueous and ionic liquid environments. Moreover, in a pioneering study on another relatively rigid, conjugated redox system, an oligoaniline contacted to the gold electrodes by thiol groups, it was found that this exhibited a peak in the molecular conductance at around the value of

the redox potential for the oxidation of the oligoaniline from its insulating (leucoemeraldine) to its conducting (emeraldine) form in aqueous electrolyte (0.05 M H<sub>2</sub>SO<sub>4</sub>).<sup>24</sup>

The vast majority of electrochemical single molecule gating studies have been performed with gold electrodes. The reason for this is that defined surface electrochemistry can be achieved with gold electrodes with a relatively wide variety of stable surface anchoring groups and importantly gold is oxide free over a reasonably wide potential window and it is easy to prepare. However, there are good reasons for developing other contacting materials. These include analysis of charge transport mechanisms with other contacts presenting different Fermi levels, level alignment and electronic density of states, and exploiting magnetic properties and spin-dependent transport through the use of ferromagnetic contacts. We have been endeavoring, with our collaborators Brooke and Schwarzacher in Bristol and Mao in Xiamen to extend the range of metals available for single molecule electrochemical gating studies. We showed that single molecule measurements could be made with cobalt contacts through the use of electroplating and ionic liquids.<sup>25</sup> This study used conventional electroplating to deposit high quality cobalt thin films on an underlying gold substrate. However, due to the sensitivity of cobalt to surface oxidation, ionic liquids were then employed as media for the removal of the surface oxide by electroreduction, followed by self-assembly of the target molecules in the same medium. The resulting molecular monolayers were shown to be of good quality as assessed by infrared spectroscopy and electrochemical characterization. Using STM, with cobalt tips, the conductance of cobalt | ODT | cobalt junctions (ODT=1,8-octanedithiol) was determined.<sup>25</sup> The molecular conductance value measured for the Co/ODT/Co junction was found to be similar to those of Au/ODT/Au and Co/ODT/Au junctions. This was attributed to the relatively small difference in work function of cobalt and gold, in combination with the relatively large gap between the metal Fermi energy and the frontier orbitals of ODT.<sup>25</sup>

Recently, single molecule electrochemical gating studies have been performed with nickel surfaces and nickel STM tips for the archetypal 4,4'-bipyridine system, by our collaborators in Bristol, Brooke and Schwarzacher.<sup>26</sup> Through control of the surface preparation, electrode potential and surface pH,

the nickel contacts could be maintained oxide-free in the 4-electrode bipotentiostatic STM-BJ setup.<sup>26</sup> In this way electrochemical gating of nickel | 4,4'-bipyridine | nickel junctions could be studied, and the importance of spin-polarized Ni d-electrons in charge transport was determined.<sup>26</sup> Figure 14 shows a comparison between conductance histograms for this system using nickel or gold electrodes. Both the conductance (left) and electrochemical gating (right) are enhanced with the oxide-free nickel electrodes. Note that the mechanism of charge transport here is phase-coherent tunneling of electrons through the LUMO tail of the 4,4'-bipyridine molecular bridge. As the electrode potential is adjusted to more negative values, the energy alignment between the LUMO and the metal Fermi energies becomes closer, in other words the Fermi energy position climbs up the molecular LUMO tail. This non-resonant mechanism, in which the molecular bridge does not change redox state, can be well-represented by DFT transport computations in which the LUMO to Fermi level energy spacing can be adjusted to mimic the electrochemical gating effect.<sup>26</sup> The ab-initio transport computations presented in this paper theoretically reproduce the higher conductance and stronger gating for the nickel | 4,4'-bipyridine | nickel junctions and show that spin-polarized d-electrons mediate charge transport through these junctions. The junction current is highly spin-polarized due to this hybridization of the nickel d band and the frontier LUMO orbitals of the 4,4'-bipyridine.<sup>26</sup>

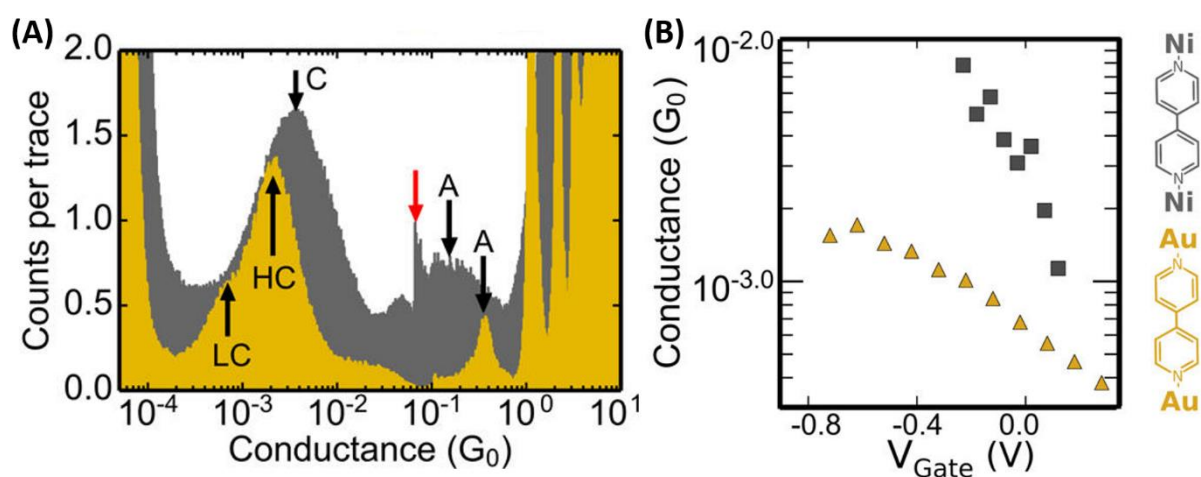


Figure 14. (A) Conductance histograms recorded for 4,4'-bipyridine under electrochemical conditions with either Au or Ni electrodes as marked. Molecular conductance peaks are between  $\sim 10^{-2} - 10^{-3} G_0$ . (B) Corresponding plots of molecular conductance versus electrochemical gating voltage. Reprinted with permission from ref. <sup>26</sup>. Copyright 2014 American Chemical Society.

In summary, STM based techniques for studying charge transfer across single molecule bridges in electrochemical environments have been valuable tools in nanoelectrochemistry and modern electrochemical surface science, in particular in advancing the understanding of charge transfer across redox active molecular bridges. Over the last decade major advances, by us and other groups, have been made in understanding charge transfer mechanisms, ranging from phase-coherent transport mechanisms to electrochemical hopping-type mechanisms. In other works, electrochemical redox switching has also proved to be valuable for analyzing quantum interference phenomena in molecular wires.<sup>27,28</sup> New methods of contacting single molecules within nanoelectrochemical junctions have also been devised which are able to enhance both conductance and single molecule electrochemical gating.<sup>26,29,30</sup> STM based single molecule electrical methods have also been successfully applied in ionic liquid electrolytes, which has enabled larger electrode potential windows to be employed, thereby allowing electrochemical gating across multiple molecular redox states to be established.<sup>1,13,15,16</sup> Ionic liquids have also been shown to promote strong gate coupling making them particularly valuable for studying single molecule field effect transistor effects.<sup>1,13</sup> The majority of such studies to date have employed gold electrodes, but recently it has become possible to study single molecule electrochemical gating with nickel electrodes.<sup>26</sup> This opens up new opportunities for coupling molecular spintronics and nanoelectrochemistry and also points towards future opportunities for investigations with other contacts such as semiconductor electrodes.

## Biographical Information

**Richard Nichols** received his Ph.D. degree in chemistry at the University of Southampton in 1989. He received the 2003 Tajima prize from the International Society of Electrochemistry, he was elected a Fellow of the International Society of Electrochemistry in 2008 and he was awarded the Geoffrey Barker Medal in 2016. Since 2000 he has been developing techniques with Higgins for the measurement of molecular electrical properties.

**Simon Higgins** received his Ph.D. degree in chemistry at the University of Southampton in 1984. His key research interests are in organic and molecular electronics. His most recent efforts have focussed on structure-property relations in molecular electronics.

## REFERENCES

- (1) Kay, N. J.; Higgins, S. J.; Jeppesen, J. O.; Leary, E.; Lycoops, J.; Ulstrup, J.; Nichols, R. J. Single-Molecule Electrochemical Gating in Ionic Liquids. *J. Am. Chem. Soc.* **2012**, *134*, 16817-16826.
- (2) Kubatkin, S.; Danilov, A.; Hjort, M.; Cornil, J.; Bredas, J. L.; Stuhr-Hansen, N.; Hedegard, P.; Bjornholm, T. Single-electron transistor of a single organic molecule with access to several redox states. *Nature* **2003**, *425*, 698-701.
- (3) Xu, B. Q.; Tao, N. J. J. Measurement of single-molecule resistance by repeated formation of molecular junctions. *Science* **2003**, *301*, 1221-1223.
- (4) Xiao, X. Y.; Xu, B. Q.; Tao, N. J. Measurement of single molecule conductance: Benzenedithiol and benzenedimethanethiol. *Nano Lett.* **2004**, *4*, 267-271.
- (5) Haiss, W.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Hobenreich, H.; Schiffrin, D. J.; Nichols, R. J. Redox state dependence of single molecule conductivity. *J. Am. Chem. Soc.* **2003**, *125*, 15294-15295.



- (6) Haiss, W.; Nichols, R. J.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Schiffrin, D. J. Measurement of single molecule conductivity using the spontaneous formation of molecular wires. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4330-4337.
- (7) Leary, E.; Hobenreich, H.; Higgins, S. J.; van Zalinge, H.; Haiss, W.; Nichols, R. J.; Finch, C. M.; Grace, I.; Lambert, C. J.; McGrath, R.; Smerdon, J. Single-Molecule Solvation-Shell Sensing. *Phys. Rev. Lett.* **2009**, *102*, 086801.
- (8) Xia, J. L.; Diez-Perez, I.; Tao, N. J. Electron transport in single molecules measured by a distance-modulation assisted break junction method. *Nano Lett.* **2008**, *8*, 1960-1964.
- (9) Peng, Z.-L.; Chen, Z.-B.; Zhou, X.-Y.; Sun, Y.-Y.; Liang, J.-H.; Niu, Z.-J.; Zhou, X.-S.; Mao, B.-W. Single Molecule Conductance of Carboxylic Acids Contacting Ag and Cu Electrodes. *J. Phys. Chem. C* **2012**, *116*, 21699-21705.
- (10) Zhou, X.-S.; Liang, J.-H.; Chen, Z.-B.; Mao, B.-W. An electrochemical jump-to-contact STM-break junction approach to construct single molecular junctions with different metallic electrodes. *Electrochem. Commun.* **2011**, *13*, 407-410.
- (11) Wang, Y.-H.; Zhou, X.-Y.; Sun, Y.-Y.; Han, D.; Zheng, J.-F.; Niu, Z.-J.; Zhou, X.-S. Conductance measurement of carboxylic acids binding to palladium nanoclusters by electrochemical jump-to-contact STM break junction. *Electrochim. Acta* **2014**, *123*, 205-210.
- (12) Leary, E.; Higgins, S. J.; van Zalinge, H.; Haiss, W.; Nichols, R. J.; Nygaard, S.; Jeppesen, J. O.; Ulstrup, J. Structure-property relationships in redox-gated single molecule junctions - A comparison of pyrrolo-tetrathiafulvalene and viologen redox groups. *J. Am. Chem. Soc.* **2008**, *130*, 12204-12205.
- (13) Osorio, H. M.; Catarelli, S.; Cea, P.; Gluyas, J. B. G.; Hartl, F.; Higgins, S. J.; Leary, E.; Low, P. J.; Martin, S.; Nichols, R. J.; Tory, J.; Ulstrup, J.; Vezzoli, A.; Milan, D. C.; Zeng, Q. Electrochemical Single-Molecule Transistors with Optimized Gate Coupling. *J. Am. Chem. Soc.* **2015**, *137*, 14319-14328.

- (14) Chappell, S.; Brooke, S.; Nichols, R. J.; Kershaw Cook, L. J.; Halcrow, M.; Ulstrup, J.; Higgins, S. J. Evidence for a hopping mechanism in metal | single molecule | metal junctions involving conjugated metal–terpyridyl complexes; potential-dependent conductances of complexes  $[M(\text{pyterpy})_2]^{2+}$  ( $M = \text{Co}$  and  $\text{Fe}$ ;  $\text{pyterpy} = 4'-(\text{pyridin-4-yl})-2,2':6',2''\text{-terpyridine}$ ) in ionic liquid. *Faraday Discuss.* **2016**, in press (DOI: 10.1039/C1036FD00080K).
- (15) Albrecht, T.; Moth-Poulsen, K.; Christensen, J. B.; Hjelm, J.; Bjornholm, T.; Ulstrup, J. Scanning tunneling spectroscopy in an ionic liquid. *J. Am. Chem. Soc.* **2006**, *128*, 6574-6575.
- (16) Kay, N. J.; Nichols, R. J.; Higgins, S. J.; Haiss, W.; Sedghi, G.; Schwarzacher, W.; Mao, B.-W. Ionic Liquids As a Medium for STM-Based Single Molecule Conductance Determination: An Exploration Employing Alkanedithiols. *J. Phys. Chem. C* **2011**, *115*, 21402-21408.
- (17) Schmickler, W.; Widrig, C. The investigation of redox reactions with a scanning tunneling microscope - experimental and theoretical aspects. *J. Electroanal. Chem.* **1992**, *336*, 213-221.
- (18) Schmickler, W.; Tao, N. J. Measuring the inverted region of an electron transfer reaction with a scanning tunneling microscope. *Electrochim. Acta* **1997**, *42*, 2809-2815.
- (19) Nichols, R. J.; Higgins, S. J.: Single Molecular Electrochemistry within an STM. In *Electrocatalysis*; Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2013; pp 99-136.
- (20) Zhang, J.; Kuznetsov, A. M.; Medvedev, I. G.; Chi, Q.; Albrecht, T.; Jensen, P. S.; Ulstrup, J. Single-molecule electron transfer in electrochemical environments. *Chem. Rev.* **2008**, *108*, 2737-2791.
- (21) Haiss, W.; Albrecht, T.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Hoebenreich, H.; Schiffrin, D. J.; Nichols, R. J.; Kuznetsov, A. M.; Zhang, J.; Chi, Q.; Ulstrup, J. Single-molecule conductance of redox molecules in electrochemical scanning tunneling microscopy. *J. Phys. Chem. B* **2007**, *111*, 6703-6712.

- (22) Zhang, W.; Gan, S.; Vezzoli, A.; Davidson, R. J.; Milan, D. C.; Luzyanin, K. V.; Higgins, S. J.; Nichols, R. J.; Beeby, A.; Low, P. J.; Li, B.; Niu, L. Single-Molecule Conductance of Viologen–Cucurbit[8]uril Host–Guest Complexes. *ACS Nano* **2016**, *10*, 5212–5220.
- (23) Zhou, X.-S.; Liu, L.; Fortgang, P.; Lefevre, A.-S.; Serra-Muns, A.; Raouafi, N.; Amatore, C.; Mao, B.-W.; Maisonhaute, E.; Schoellhorn, B. Do Molecular Conductances Correlate with Electrochemical Rate Constants? Experimental Insights. *J. Am. Chem. Soc.* **2011**, *133*, 7509–7516.
- (24) Chen, F.; He, J.; Nuckolls, C.; Roberts, T.; Klare, J. E.; Lindsay, S. A molecular switch based on potential-induced changes of oxidation state. *Nano Lett.* **2005**, *5*, 503–506.
- (25) Catarelli, S. R.; Higgins, S. J.; Schwarzacher, W.; Mao, B.-W.; Yan, J.-W.; Nichols, R. J. Ionic Liquid Based Approach for Single-Molecule Electronics with Cobalt Contacts. *Langmuir* **2014**, *30*, 14329–14336.
- (26) Brooke, R. J.; Jin, C.; Szumski, D. S.; Nichols, R. J.; Mao, B.-W.; Thygesen, K. S.; Schwarzacher, W. Single-Molecule Electrochemical Transistor Utilizing a Nickel-Pyridyl Spinterface. *Nano Lett.* **2015**, *15*, 275–280.
- (27) Darwish, N.; Diez-Perez, I.; Da Silva, P.; Tao, N. J.; Gooding, J. J.; Paddon-Row, M. N. Observation of Electrochemically Controlled Quantum Interference in a Single Anthraquinone-Based Norbornylogous Bridge Molecule. *Angew. Chem. Int. Ed.* **2012**, *51*, 3203–3206.
- (28) Baghernejad, M.; Zhao, X. T.; Orso, K. B.; Fueg, M.; Moreno-Garcia, P.; Rudnev, A. V.; Kaliginedi, V.; Vesztergom, S.; Huang, C. C.; Hong, W. J.; Broekmann, P.; Wandlowski, T.; Thygesen, K. S.; Bryce, M. R. Electrochemical Control of Single-Molecule Conductance by FermiLevel Tuning and Conjugation Switching. *J. Am. Chem. Soc.* **2014**, *136*, 17922–17925.
- (29) Hines, T.; Diez-Perez, I.; Nakamura, H.; Shimazaki, T.; Asai, Y.; Tao, N. Controlling Formation of Single-Molecule Junctions by Electrochemical Reduction of Diazonium Terminal Groups. *J. Am. Chem. Soc.* **2013**, *135*, 3319–3322.

(30) Li, Z.; Li, H.; Chen, S.; Froehlich, T.; Yi, C.; Schoenenberger, C.; Calame, M.; Decurtins, S.; Liu, S.-X.; Borguet, E. Regulating a Benzodifuran Single Molecule Redox Switch via Electrochemical Gating and Optimization of Molecule/Electrode Coupling. *J. Am. Chem. Soc.* **2014**, *136*, 8867-8870.